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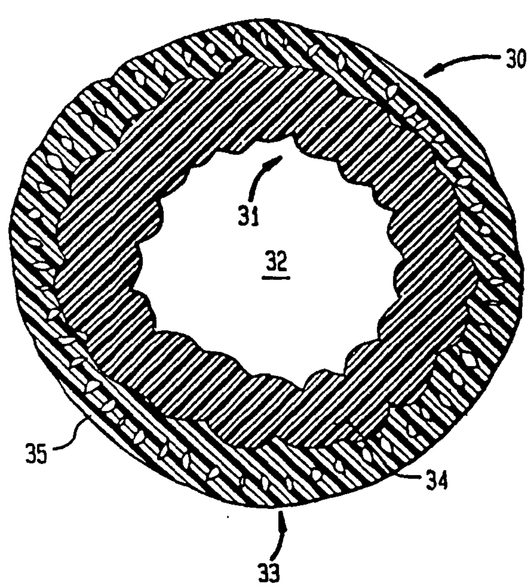
(54) Title: HOLLOW FIBER MEMBRANE AND BRAIDED TUBULAR SUPPORT THEREFOR



(57) Abstract: An asymmetric membrane comprising a tubular polymer film in combination with a tubular braid on which the film is supported, requires the braid be macroporous and flexible, yet sufficiently strong to withstand continuous flexing, stretching and abrasion during use for microfiltration (MF) or ultrafiltration (UF). The specifications for a braid of a long-lived membrane are provided. A membrane is formed by supporting a polymer film in which particles of calcined α-alumina are dispersed, on the defined tubular braid.

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equipment from commercially available yarn, there were numerous "breaks" in the fiber; also, accumulation of clumps of broken filaments, referred to as "fuzz", braided into the cylindrical wall of the braid, resulted in weak spots in the polymer film coated onto the surface; and broken filaments, referred to as "whiskers", protruding from the surface of the tubular braid, resulted in too-thick domains of polymer which were concentrated around the whiskers; and, when the domain was not too-thick, whiskers have a proclivity to initiate pin-holes.

Further, if the open weave of the braid provided either too high or too low a braid porosity as measured by resistance to air flow, the fiber membrane formed was unusable in a commercial installation. Too open a weave resulted in the braid being embedded, that is, enclosed by and firmly fixed in the polymer which also infiltrates into the bore of the braid; thus, too open a weave results in greatly reduced permeability. Too tight a weave results in the polymer not being anchored sufficiently well on the surface; this increases the likelihood that, in service, the polymer film will be peeled from the braid. When operating flux was excellent, portions of the polymer film were sometimes found to have been peeled away when the fibers were back-washed with clean water or other fluid medium, whether water or permeate, under pressure; or portions of the film were "blown off" the surface of the fibers when their lumens were pulsed with air under pressure. Even with the best braid produced under controlled conditions, shrinkage during usage in an aqueous medium varied unpredictably. This resulted in taut fibers which were prematurely fouled because they were unable to move sufficiently to stay clean or rub against each other. If too taut, the fibers are broken before they are fouled, or torn from potting resin in the header. Particularly because it is essential for best performance, and to shed contaminants from the surfaces of the hollow fiber membranes, that a skein of fibers operate with "slack" fibers, the structure of the braid needs to survive repetitive twisting, and it was not known what physical characteristic(s) of the braid was conducive to such survival. A cylindricity less than 0.8 resulted in a polymer film with unacceptable variations in thickness resulting in non-uniform flux

membrane-forming polymer is dissolved, the braid having a stable heat-pre-shrunk length which is in the range from about 1% to 20% less than its un-shrunk length, preferably so that, irrespective of the material forming the fibers, when the pre-shrunk braid is stretched longitudinally, it has "give", that is, the extension at break is at least 10%, preferably in the range from 10% to 30%, and more preferably about 20%.

It is a specific object of this invention to provide a heat-pre-shrunk tubular braid made with specified patterns, using carriers carrying yarn having defined number of filaments, ends, denier, and picks, under conditions which control the porosity (measured as permeability to air) of the braid, such controlled porosity serving to anchor a polymer film non-removably on the surface of the tubular braid.

It is another specific object of this invention to provide, in a flexible macroporous tubular braid support for an outside-in hollow fiber asymmetric membrane having a tubular film of synthetic resinous material supported on the outer circumferential surface of the braid without the support being embedded in a thin film having a wall thickness of less than 0.2 mm, the improvement comprising, 16 to 60 separate yarns, each on its own carrier, each yarn being multifilament 150 to 500 denier (g/9000 meters) yarn, each multifilament being made with from 25 to 750 filaments, each filament being from 0.5 to 7 denier. From 1 to 3 multifilament ends constitute a yarn, and the individual ends are most preferably not plied together, but lie linearly adjacent to each other until taken up in the "fell" of the braid being woven. The braid being woven has from 30 to 45 picks (crosses/inch). The higher the denier of the filaments, the fewer the filaments used, but the braid wall thickness is maintained in the range from about 0.2 mm but less than three times the diameter of the yarn from which the braid is woven, preferably less than 1.0 mm. The air permeability of the braid of synthetic resinous yarn is in the range from about 1 to 10 $cc/sec/cm^2$ at a differential pressure of 1.378 kPa (0.2 psi); and the moisture regain is in the range from about 0.2% to 7% by weight (wt). The finished fiber membrane is coated with a thin polymer film having a thickness in the range from 0.05 mm to 0.3 mm, most prefer-

is incorporated by reference thereto as if fully set forth herein. A preferred tubular braid is woven with yarn, the denier of which is chosen with consideration of the outside diameter of the braid on which the polymer film is to be coated, and whether the membrane is to be used for MF or UF. A desirable air-permeability for a UF membrane to provide drinking water, is in the range from about 5 to 25 LMH/kPa (liters/m^2/kPa/hr) or 20 to 100 GFD/psi (gals/ft^2/day/psi), preferably from about 7.4 to 18.5 LMH/kPa (30 to 75 GFD/psi), measured with RO (reverse osmosis) water; a desirable permeability for a MF membrane used to filter municipal sewage and provide clean water is in the range from 10 to 50 LMH/kPa (40 to 200 GFD/psi), typically about 12.5 to 25 LMH/kPa (50 to 100 GFD/kPa), measured with RO water. A typical defect-free fiber has a bubble point in the range from about 140 to 280 kPa (20 to 40 psi). For a UF membrane it is desirable to have a bubble point in the range from 13 to 40 kPa (2 to 6 psi), preferably about 35 kPa (5 psi) to emphasize the importance of a defect in a fiber; for a MF membrane it is desirable to have a bubble point in the range from 6 to 20kPa (1 to 3 psi), preferably about 13 kPa (2 psi), for the same reason.

The structure of the tubular braid is determined by the machine used to weave the braid which is formed of intertwined, spiral yarns so that its thickness is less than three yarn diameters, and the yarn orientation is helical. The braided tube my be woven on either vertical or horizontal tubular braiding machines, the former being preferred. A machine includes a track plate provided with intertwining tracks, plural tube or bobbin carriers for the yarn capable of moving counterclockwise or clockwise along the tracks for braiding, a former and a take-up device. Bobbins are flanged tubes used for yarns which are difficult to handle. Yarns from bobbins mounted on the bobbin carriers are braided as they are guided to a gathering guide disposed above the center of the disk. Each bobbin carrier is rotated by a drive gear disposed under the track plate while it moves along the tracks. The ratio between the moving speed of the bobbin carriers and the braid drawing speed can be changed by changing the gear ratio, so that the braids may differ from each other in the angle of the strands. Different interlacings, or weave patterns,

overlying polymer film. Undue stress on the braid results in breakage, typically near the ends of the fiber membranes, where they are potted in headers; and undue stress on the polymer film diminishes its adherence and increases its susceptibility to peeling from, or sloughing off the surface of the braid.

Though a "shrink test" is commonly conducted on yarns by heat shrinking in water at 98°C via a Texurmat boil off; or, in dry air at 177°C with 0.045 gf/dtex tension for 2 min (DuPont); or, in dry air at 190°C with 0.135 gf/d for 30 sec (Monsanto), to date there has been no reason to heat pre-shrink any tubular braid of synthetic resin, prior to its being coated with polymer. More particularly, since a braid woven with glass fiber is essentially non-heat-shrinkable, there has been no reason to provide a stable length of a polyester or nylon tubular braid by pre-shrinking it so that its shrunk length is about 84% of its pre-shrunk length at the same time ensuring that the braid retains at least 95% of its tensile strength.

Heat-shrinking in dry air, referred to as Testrite tests, of polyester and polyamide tubular braids to obtain most preferably from about 16% to 18% shrinkage, may be acheived in an electric furnace at 232°C for 29 sec.

The denier of the yarn and structural characteristics of the braid determine the liquid and gas permeability. The liquid permeability of the braid is at least one order of magnitude (that is, more than 10 times) greater than the permeability of the polymer film. Thus the weave of the braid is so open that it presents an insubstantial barrier to gas flow.

Permeability to air of preferred polyester ("PE") and nylon ("NY") braids, determined by ASTM Standard "Air Permeability of Textile Fabrics D 737-96" are measured for a differential pressure of 1.38 kPa (0.2 psi). These are listed in the following Table 1 under "@0.2 kPa". Also listed are permeabilities "@0.02 kPa" (0.029 psi) which are obtained by extrapolation of the data curve obtained with measurements at 0.2 kPa, in the appropriate range:

Tester" (LR K5 with a 50 N load cell) having a "German Wheel" (the "Tester" for brevity).

The "German Wheel" is used to execute a peel test of a coating on a flexible substrate, at 90° to the surface of the substrate. Each sample is especially prepared according to the standard being used. The German Wheel consists of a free running axle mounted wheel and a yoke which receives the wheel and connects it to the load to execute a test. The face of the wheel contains a sharp angled slot into which one end of the coated substrate is inserted and folded back against the sharp edge. This creates a mechanical lock which holds the sample tight as its length is drawn, coating side up, around the periphery of the wheel and passed through a locking clamp. The clamp site is just beyond a region where the coating tab length has been separated from the substrate. Thus the flexible substrate is clamped and the coating tab length hangs freely, in front of the clamp.

All tests are done on wet membranes, by slitting a six inch (6") wet membrane longitudinally. One and one-half inch (1.5") of membrane is peeled from the braid. A bare one inch (1") section of braid is inserted into the angle slot and the rest of the braid is bent around the wheel such that the longitudinal slot is facing toward the wheel surface. The angled slot anchors one end and the loose end is placed in the floating clamp and tightened. Any slack is removed by the sample tensioning screw.

The loose end of the peeled section of membrane is placed in the upper clamp of the Tester. Four inches of membrane are pulled off the braid at a rate of 100 mm/min. The German wheel rotates freely to keep the angle of peel constant. The material tester outputs a graph showing the amount of force required to peel the membrane off the substrate. The results of the samples are averaged together and plotted on a graph. The average maximum force of approximately the two inch section is recorded.

Tensile Strength of Each Sample is conducted as follows:

The wet samples of membrane obtained from the Peel Test are placed in the clamps of the Tester. The clamps are placed one inch apart. The

leaving the rounding orifice. As the dope-coated braid is advanced through the sizing orifice, it dresses the outside diameter of the polymer-coated surface to provide the dope with a desired wall thickness, which upon being coagulated, yields a thin film membrane which is no more than 0.1 mm thick.

The base 25 is provided with a lower port 21 and an upper port 26 each in open communication with the stepped bores 22 and 23, so that dope introduced into the port 21 can flow into the reservoir formed around the inner barrel 12, by the stepped bores 22 and 23, and travel longitudinally axially in the direction in which the braid is drawn through the larger bore 22, and the smaller bore 23 displacing air as the reservoir fills. When the dope having filled the reservoir flows out of the top port 26, it is plugged. The base 25 is removably secured with through-bolts (not shown) through the base 25 to a radially extending mounting flange 29 having a longitudinal body portion 29'. The body portion 29' is provided with an internally threaded axial bore so that the body portion 29' can be secured coaxially in position, aligning the rounding orifice 14 and the sizing orifice 24. By increasing or decreasing the number of turns of the body portion 29' the distance between the mouth of the orifice 14 and the orifice 24 can be varied. This distance is adjusted, depending upon the rate at which the braid is pulled through, the viscosity of the dope, and the thickness of the film of dope to be coated on the braid before it is immersed in the coagulant. In all cases, the distance is adjusted by trial and error, to provide a film of dope on the circumferential outer surface of the braid only sufficient to coat the braid superficially, and not enough to embed the braid in the film.

To draw the braid through the orifice 24, a longitudinal tension is maintained on the braid of at least 1 Newton but not enough to distort the voids in the braid so badly that they cannot return to an equilibrium state as they are being coated with dope. Because the braid is not embedded in the viscous polymer solution, only the outer surface of the braid is contacted with the dope so as to provide the braid with a dope- and polymer-coated outer surface.

It will now be evident that the coating nozzle 10 is a special-purpose

between outer layer 36 and inner layer 38, as schematically illustrated in greater detail in Fig 4. The skin is a very thin dense layer of polymer formed as the dope contacts the coagulant. By reason of the manner in which the skin and each layer is formed from the same polymer, the layers have, in a radially inward direction from under the skin to the braided yarn 39 which defines the bore 32, progressively larger pores. As shown in Fig 4, each "end" 39 or yarn consists of a multiplicity of filaments 39', and the circumferential surface of the interwoven strands of yarn does not provide a smoothly cylindrical surface. The skin is generally thinner and the pores for a MF membrane are larger than those of a UF membrane made from the same polymer. The measured skin thickness (by electron microscopy) for particular films made for the braided membrane, is given below to appreciate its thickness in relation to the pores of the layers. The approximate ranges of sizes of the pores for preferred MF and UF membranes are given below:

Table 2

	MF, μm	UF, μm
Skin 35, thickness	0.1 - 1.5	1 - 4
Outer layer 36, avg pore diam	0.5-1.0	0.5-2
Intermediate transport layer 37*	2 - 6	5 - 10
Inner layer 38, avg pore diam	10 - 40	10 - 150

*average pore diameter

In membranes, in general, the thickness of the skin is small relative to the thickness of the layers. The skin is thicker in a UF membrane than in a MF membrane, and it would be even thicker in a RO membrane (not measured). Though Fig 4 is not to scale, by reason of the manner in which the membrane is formed, the thickness of the outer layer is generally smaller than that of the transport layer, which in turn, is not as thick as the inner layer.

The approximate thickness of each layer in a MF and UF braided membrane are given in the following Table 3.

The braids differed as follows:

	Braid A	Braid B
Yarn Denier	315	420
Filaments	68	68
Denier/filament	4.6	6.2
Ends	1	1
Picks	44	44
Cylindricity	0.9	0.9
Mean outside diam.	1.88 mm	2.01 mm
Mean inside diam.	0.86 mm	1.06 mm
Shrinkage	3.4%	3.4%
Breaking strength, lb-f	5.93	7.68
Button**	2.15 mm	2.53 mm

**the inside diameter of a finishing die through which the coated braid is passed.

Upon being tested for filtration, coated Braid B provided a permeability twice that of coated Braid A. Upon examination of the coated braids, it is found that Braid A, made with lower denier yarn, gave a "looser" braid which allowed the dope to penetrate to the inner wall of the braid, embedding it, and leaving little on the outer surface, as is evident from the following:

	Braid A	Braid B
Coated mean outr diam.	1.89 mm	2.15 mm
Thickness of coating	0.005 mm	0.070 mm
Mean wall thickness	0.520 mm	0.475 mm
Flux @ 15 psi	171.9 usgfd	383 usgfd

A photograph of a cross-section of the braided MF membrane, made with an electron microscope, shows the film membrane overlying the braid to be about 0.05 mm thick and the braid is not embedded in the film. The thickness of the skin 35, and each individual layer 36-38 will depend upon the

amount in the range from 400 to 450 m^3/hr is provided at the base of each skein. After six months service under usual operating conditions and identical back-flushing procedures, it was found that every skein made with glass fiber braid had suffered from 2 to 20 broken fibers.

When skeins made with fibers of polyester braid are placed in the same service as the fibers of glass fiber braid above, under identical operating conditions and the same back-flushing procedures, it was found that after six months service, not a single fiber of polyester braid was broken.

Example 3

A dope is made up similar to the PVDF-in-NMP solution used in Example 1 hereabove, except that it is made up with the following components in the relative amounts (parts by weight) set forth: N-methyl-2-pyrrolidone (NMP) 82; polyvinylidene fluoride (PVDF) 15; calcined α-alumina particles ("α-Al") 2; 50% hydrolyzed polyvinyl acetate (HPVA) 1; for a total of 100 parts.

70 g of calcined α-Al particles having an average primary particle size of about 0.4 μm are weighted in a flask to which 2787 g of NMP is added and thoroughly mixed in a Sonicator® for at least 1.5 hr, to ensure that agglomerates of primary particles are broken up so as to form a suspension in which individual primary particles are maintained in spaced apart relationship with each other in the NMP. The suspension is milky white, the white color being contributed by the white calcined α-Al. To this suspension is slowly added 525 g of PVDF having a number average mol wt of about 30,000 Daltons while stirring at high speed until addition of the PVDF is complete. During the addition of the PVDF the milky white color of the suspension changes first to pink, then to yellowish brown, at the end to grey/brown. Since PVDF dissolved in NMP produces no color change, and the milky white color of the suspension is attributable to the α-Al particles, the changes in color provide evidence of a reaction between the calcined α-Al or a base present in the calcined alumina.

When the grey/brown color of the NMP/PVDF/α-Al complex in suspension is stable and does not change upon standing for a sustained period in

CLAIMS

We claim:

1. A liquid separation asymmetric membrane comprising a tubular braid support synthetic resinous yarn woven so that said braid has a stable heat-pre-shrunk length which is in the range from about 1% to 20% less than its unshrunk length and an air permeability less than 10 cc/sec/cm^2 at 1.378 kPa.

2. The tubular braid support of claim 1 wherein said braid, stretched longitudinally, has an extension at break of at least 10%.

3. The tubular braid support of claim 1 wherein said braid is woven with from 16 to 60 carriers, each using multifilament 150 to 500 denier yarn, each multifilament being made with from 25 to 750 filaments, each filament being from 0.5 to 7 denier, said yarn comprising from 1 to 3 multifilament ends.

4. The tubular braid support of claim 3 wherein said braid has from 30 to 45 picks (crosses/inch).

5. The tubular braid support of claim 4 wherein said filaments formed from a synthetic resin selected from the group consisting of polyester, polyamide, polyolefin, polyamine, polyurethane, polysulfone and cellulose acetate.

6. The tubular braid support of claim 5 wherein said braid has a wall thickness in the range from 0.2 mm to less than three times the thickness of said yarn.

7. The tubular braid support of claim 5 wherein said synthetic resin is selected from the group consisting of polyester and polyamide, said braid has sufficient strength to exhibit a load at break of least 50 lb-force.

(i) a macroporous foraminous tubular support means having an outer surface; and,

(ii) a polymeric film of a reaction product of (a) a complex of polyvinylidene difluoride (PVDF) with calcined α-alumina particles, and (b) a hydrophilic polymer adapted to impart hydrophilicity to said membrane;

said particles having a primary particle size in the range from about 0.1 μm to 5 μm being present in an amount at least 1 percent by weight, but less than 50 percent by weight, of said film;

said film being supported by said outer surface, and said film having a peripheral barrier layer or "skin" integral with successive microporous layers having pores having an average diameter in the range from about 0.01 μm to about 0.3 μm, in open communication with each other,

the improvement comprising,

a flexible macroporous tubular braid support comprising from about 16 to 60 separate yarns, each on its own carrier, each yarn using multifilament 150 to 500 denier (gm/9000 meters) yarn, each multifilament being made with from 25 to 750 filaments, each filament being from 0.5 to 7 denier, said braid being woven with from 1 to 3 multifilament ends at from 30 to 45 picks (crosses/inch).

15. The hollow fiber of claim 14 wherein said macroporous foraminous tubular support means support means has a stable heat-pre-shrunk length which is in the range from about 1% to 20% less than its unshrunk length and an air permeability less than 10 cc/sec/cm^2 at 1.378 kPa.

16. The hollow fiber of claim 15 wherein said filaments are formed from a synthetic resin selected from the group consisting of polyester and polyamide.

17. The hollow fiber of claim 15 wherein said braid, stretched longitudinally, has an extension at break in the range from 10% to 30%.

18. The hollow fiber of claim 16 wherein said braid has an inside diameter

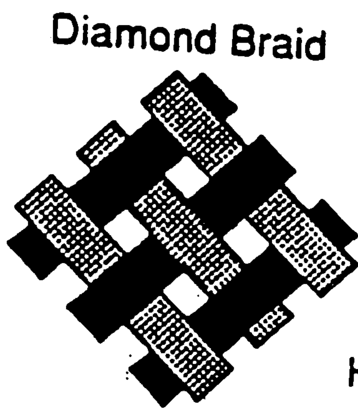

FIG. 1A

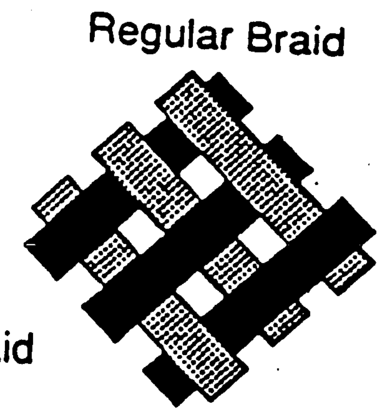

FIG. 1B

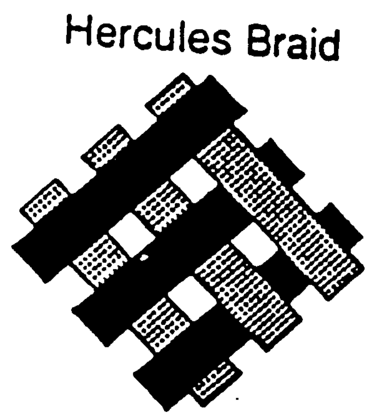

FIG. 1C

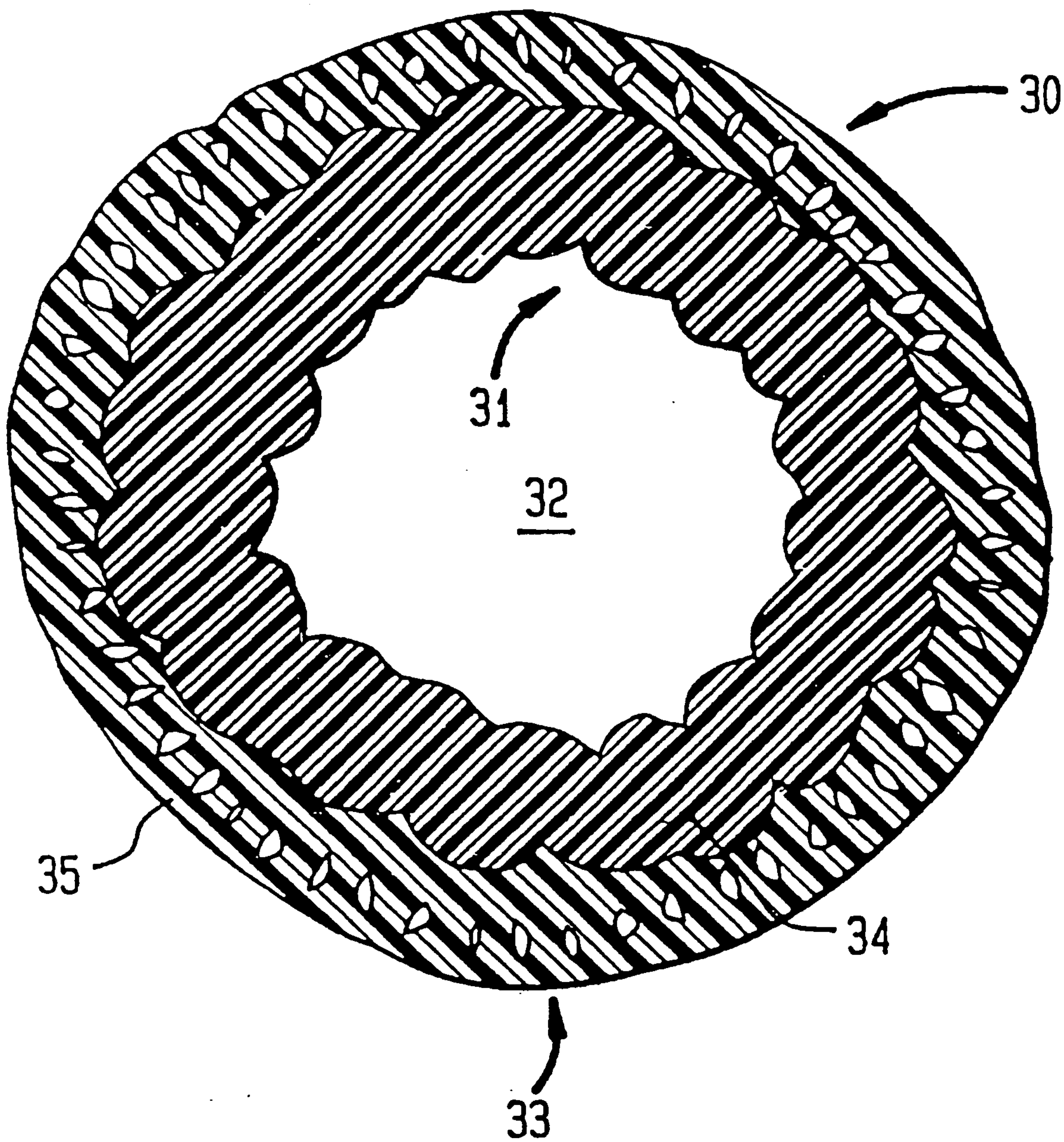

FIG. 3

INTERNATIONAL SEARCH REPORT

Inte onal Application No
PCT/CA 00/00640

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01D69/10 B01D69/08 B01D69/14 B01D71/34 C08K9/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B01D C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
WPI Data, PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
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Date of the actual completion of the international search	Date of mailing of the international search report
29 August 2000	05/09/2000

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
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